

Formation of Clusters of Interstitial Carbon Atoms in Graphite due to Deformation Interaction and their Spatial Arrangement

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Formation of clusters of interlayer interstitial carbon atoms in graphite is studied by means of molecular dynamics simulation. It is shown that the deformation potential is attractive for interstitials located in one interlayer region and repulsive for interstitials located in different interlayer regions. As a result, relatively small interstitial clusters are formed which are arranged in a checkerboard-like order.

1. Introduction

Irradiation of solids by neutrons, ions, electrons and other particles results in the formation of irradiation-induced defects. The processes of defects creation are accompanied by the processes of defects annihilation, mainly due to recombination of vacancies and interstitials. Hence, one can expect that a stationary defect state should be reached, such a state being characterized by the relatively low defect concentration n_d . However, the expected saturation of n_d is not seen in the experiment [1,2]. For example, the volume of graphite increases monotonously under irradiation up to very high doses. Hence, there exists a mechanism that prevents the recombination.

One possible explanation of recombination suppression is the formation of clusters of point defects at the sacrifice of deformation interaction [3,4]. As is known (see, e.g., [5]), interstitials stretch the lattice, while vacancies compress the lattice. The stretched domains are attractive for interstitials and repulsive for vacancies. As a result, clusters of interstitials and clusters of vacancies should be formed. The formation of such clusters has been predicted in [3,4] by the example of isotropic crystals. Spatial separation of interstitial clusters and vacancy clusters suppresses the recombination. In principle, this allows one to explain the accumulation of defects (and, hence, structural changes and swelling) up to high radiation doses.

We note that the region of deformation interaction in isotropic crystals is rather small (of the order of one atomic volume), i.e., such an interaction is point-like in the continuum limit. The range of deformation interaction in anisotropic crystals (e.g., in layered graphite) may be much longer than in isotropic ones. Indeed, interstitials placed between the graphite layers cause the strong deformation of those layers [6,7]. Hence, the formation of interstitial clusters may be expected to be more pronounced in anisotropic crystals.

Recently a number of experimental results has been obtained that lend support to the physical picture described above. In particular, it was shown experimentally and theoretically [8] that krypton atoms in graphite form clusters located between the layers. Those atoms come close together due to forces acting on them from the deformed layers. According to numerical simulations of 1, 2, and 3 krypton atoms placed into the interlayer region, the deformation forces are so strong that the distance between the krypton atoms in clusters appears to be shorter than that in the bulk krypton crystal [8].

The purpose of this work is the theoretical study of deformation interaction of interstitial carbon atoms located between the graphite layers, as well as the study of formation of interstitial clusters between several layers. As a first step, we make use of a simple model with empirical interatomic potential. By means of molecular dynamics simulations, it is shown that interstitials located between the nearest layers attract to each other. On the other hand, interstitials located between the different pairs of graphite layers (i.e., in different interlayer regions) repel each other. This repulsion sets limits on the size of interstitial clusters and prevents their transformation into "superplanes", contrary to common opinion. The relatively small interstitial clusters are arranged in a checkerboard-like order.

2. Deformation Interaction of Two Interstitial Carbon Atoms in Graphite

Numerical simulation was carried out by molecular dynamics technique making use of empirical interatomic potentials for interaction between the carbon atoms of graphite layers as well as between the interstitial carbon atoms and the atoms of graphite layers [7]. Parameters of those potentials were chosen by fitting the calculated values of interatomic distances and elastic moduli to their experimental values in defect-free graphite. Besides, the calculated value of self-energy of a single interstitial, $E_{is} = 1.8$ eV, agrees well with experimental data and theoretical estimates [6,9]. The covalent interaction between the interstitials was taken into account approximately as hard-core interaction

of solid spheres having the radius $d/2$, where $d = 1.42$ Å is the covalent bond length within graphite layers.

The simulation was carried out for the 1320-atom crystallite consisted of 6 layers, each of which included 220 carbon atoms. In order to keep the stability of the crystallite, we fixed the atoms of upper and lower layers, as well as the atoms on the peripheries of layers. All other atoms were allowed to relax after the interstitials have been inserted into the crystallite.

Fig.1 shows the results of calculation of atomic configurations (after relaxation) for the case that two interstitials are located between the nearest graphite layers (i.e., in one interlayer region) at a fixed in-plane distance r from each other. The energy U of deformation interaction was defined as follows:

$$U(r) = E(N + 2, r) - E(N + 1, \mathbf{r}_1) - E(N + 1, \mathbf{r}_2) + E(N), \quad (1)$$

where $E(N)$ is the total energy of N -atom defect-free crystallite, $E(N + 1, \mathbf{r}_1)$ and $E(N + 1, \mathbf{r}_2)$ are the total energies (after relaxation) of the crystallite containing an interstitial in the position \mathbf{r}_1 and \mathbf{r}_2 respectively, $E(N + 2, r)$ is the total energy (after relaxation) of the crystallite containing two interstitials in the positions \mathbf{r}_1 and \mathbf{r}_2 , and r is the in-plane distance between the interstitials.

The dependence of the deformation energy U on r is shown in Fig.2. One can see that U is negative at $r < 8$ Å, decreases monotonously as r decreases, and reaches the value ≈ -1 eV at $r = d$ (a small maximum $U \approx 0.03$ eV at $r \approx 10$ Å may be due to finite size effects). So, in accordance with the mechanism considered in [3], we see that a rather strong mutual attraction of interlayer interstitials does exist since it is energetically favorable for interstitials to be located in the domain of stretched lattice. Besides, the range of deformation interaction is rather long (≈ 10 Å), as would be expected for anisotropic crystals.

Fig.3 shows the results of calculation of atomic configurations (after relaxation) for the case that two interstitials are located between the different pairs of graphite layers (i.e., in different interlayer regions) at a fixed in-plane distance r from each other. The dependence of the deformation energy U on r is shown in Fig.4. One can see that U is positive at $r < 6$ Å. This corresponds to the mutual repulsion of two interstitials. Note that U increases monotonously as r decreases, and reaches the value ≈ 3 eV at $r = 0$ (a small minimum $U \approx -0.05$ eV at $r \approx 8$ Å may be due to finite size effects).

3. Formation of Clusters of Interstitial Carbon Atoms in One Interlayer Region

Since two interstitials located between the nearest graphite layers attract to each other at the sacrifice of deformation interaction, one can expect that several interstitials located in one interlayer region should come closer together and form a cluster. In order to study the dynamics of interstitial clusters formation, we performed the calculations as follows. Initially (at $t = 0$) several interstitials were randomly distributed between two layers of the crystallite. Then all atoms were allowed to relax, including the interstitials.

Fig.5 shows the dynamics of 7-interstitial cluster formation. At the first stage ($t = 200$) three clusters composed of 2, 2, and 3 interstitials are formed. At the next stage ($t = 800$) two of those clusters fuse into a 5-interstitial cluster. Finally, the 7-interstitial cluster is formed. Thus, all interstitials merge together into a single cluster due to deformation interaction. From Fig.5 one can see that a characteristic time of 2- and 3-interstitial clusters formation is an order of magnitude shorter than the time of fusion of those clusters into a larger one. This fact indicates that the mobility of a cluster decreases drastically with the number of interstitials in it.

We note that the 7-interstitial cluster has a trigonal structure, as opposed to a hexagonal structure of the graphite layer. The reason is that the interaction between the interstitials was taken into account in a rather crude way.

Similar results were obtained for several other initial distributions of interstitials in the interlayer region, as well as for different numbers of interstitials in the region. It turns out that the resulting shape of an interstitial cluster depends on the initial distribution of interstitials, while the structure of the cluster is always trigonal. It can be shown that the covalent bonding between the interstitials results in formation of a fragment of graphite layer having a hexagonal structure.

4. Formation of Clusters of Interstitial Carbon Atoms in Three Interlayer Regions

As shown above, interstitials located in one interlayer region form a large cluster. The reason is that the deformation potential is attractive for such interstitials. As the number of interstitials in the cluster increases, the cluster transforms into a new graphite layer.

However, once interstitials are created throughout the whole sample, the deformation repulsion of interstitials located in different interlayer regions should have a profound effect on the process of interstitial clusters formation. In

order to study this effect, we performed the calculations for the case that initially (at $t = 0$) as many as 39 interstitials were randomly distributed over three interlayer regions of the crystallite (with the constraint of 13 interstitials in each interlayer region).

Fig.6 shows the dynamics of interstitial clusters formation. We stress that in none of three interlayer regions do all 13 interstitials merge into a single cluster, contrary to the case of cluster formation in one interlayer region (see Fig.5). It is seen from Fig.6 that two clusters have been formed in the middle and upper regions each, while four clusters have been formed in the lower region. We stress that clusters are arranged in a checkerboard-like order. The reason is the deformation repulsion of interstitials located in different interlayer regions.

5. Conclusions

1. We have shown that there is strong deformation interaction of interstitial carbon atoms in graphite. This interaction is attractive for interstitials located in one interlayer region and repulsive for interstitials located in different interlayer regions. A characteristic value of the deformation energy U is about 1 eV. The dependence of U on the in-plane distance between two interstitials was calculated.

2. The deformation attraction of interstitial carbon atoms was demonstrated to result in formation of interstitial clusters in interlayer regions.

3. It was shown that deformation repulsion of interstitials prevents the transformation of interstitial clusters into new graphite layers because of formation of relatively small clusters arranged in a checkerboard-like order. We believe this effect to be the reason for recombination suppression in graphite because of spatial separation of interstitial clusters and vacancy clusters. This is a possible explanation for the absence of saturation of defect concentration in graphite up to high radiation doses.

Finally, it is worth noting that recently several researches [10–14] have reported STM images of defect structures on the surfaces of ion-irradiated highly-oriented pyrolytic graphite (HOPG). Analysis of published experimental results points to an important role of processes of interstitial clusters formation due to deformation interaction.

Acknowledgments

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- [1] T.Iwata and H.Suzuki, in *Proc. IAEA Symp. "Radiation Damage in Reactor Materials"*, Vienna, 1963, p.565.
 - [2] B.T.Kelly, *Irradiation Damage to Solids*, Pergamon Press, 1967 [Russian translation: Atomizdat, Moscow, 1970].
 - [3] V.F.Elesin, Dokl. Akad. Nauk SSSR, 298 (1988) 1377 [Sov. Phys. Dokl., 33 (1988) 138].
 - [4] V.F.Elesin, Pis'ma Zh. Eksp. Teor. Fiz., 59 (1994) 451 [JETP Lett., 59 (1994) 472].
 - [5] ..Kosevich, *Physical Mechanics of Real Crystals*, Naukova Dumka, Kiev, 1981 (in Russian).
 - [6] C.A.Coulson, S.Senent, M.A.Herraez, M.Leal, E.Santos, Carbon, 3 (1966) 445.
 - [7] Y.Taji, T.Yokota, T.Iwata, J. Phys. Soc. Jap., 55 (1986) 2676.
 - [8] D.Marton, K.J.Boyd, T.Lytle, J.W.Rabalais, Phys. Rev. B, 48 (1993) 6757.
 - [9] P.A.Thrower and R.M.Mayer, Phys. Stat. Sol. (a), 47 (1978) 11.
 - [10] L.Porte, M.Phaner, C.H. de Villeneuve, N.Moncoffre, J.Tousset, Nucl. Instr. Meth. Phys. Res. B, 44 (1989) 116.
 - [11] R.Coratger, A.Claverie, F.Ajuston, J.Beauvillain, Surf. Sci., 227 (1990) 7.
 - [12] L.Porte, C.H. de Villeneuve, M.Phaner, J. Vacuum Sci. Technol. B, 9 (1991) 1064.
 - [13] D.Marton, H.Bu, K.J.Boyd, S.S.Todorov, A.H. Al-Bayati, J.W.Rabalais, Surf. Sci., 326 (1995) L489.
 - [14] T.Matsukawa, S.Suzuki, T.Fukai, T.Tanaka, I.Ohdomari, Appl. Surf. Sci., 107 (1996) 227.

FIGURE CAPTIONS

Fig.1. Distortion of graphite lattice by two interstitials located between the nearest graphite layers at the in-plane distance (A) $r = 9.2 \text{ \AA}$ and (B) $r = 1.7 \text{ \AA}$ from each other.

Fig.2. Dependence of the deformation energy U on the in-plane distance r between two interstitials located between the nearest graphite layers, see Fig.1. The dots are the results of calculation. The line is a guide to the eye.

Fig.3. Distortion of graphite lattice by two interstitials located between the different pairs of graphite layers at the in-plane distance (A) $r = 9.8 \text{ \AA}$ and (B) $r = 0$ from each other.

Fig.4. Dependence of the deformation energy U on the in-plane distance r between two interstitials located between the different pairs of graphite layers, see Fig.3.

Fig.5. Dynamics of interstitial cluster formation in one interlayer region. Top view. Atoms of graphite layers are not shown. Time t is in arbitrary units.

Fig.6. Dynamics of interstitial clusters formation in three interlayer regions. Top view. Squares, circles, and triangles show the interstitials in lower, middle, and upper regions respectively. Atoms of graphite layers are not shown. Time t is in arbitrary units.

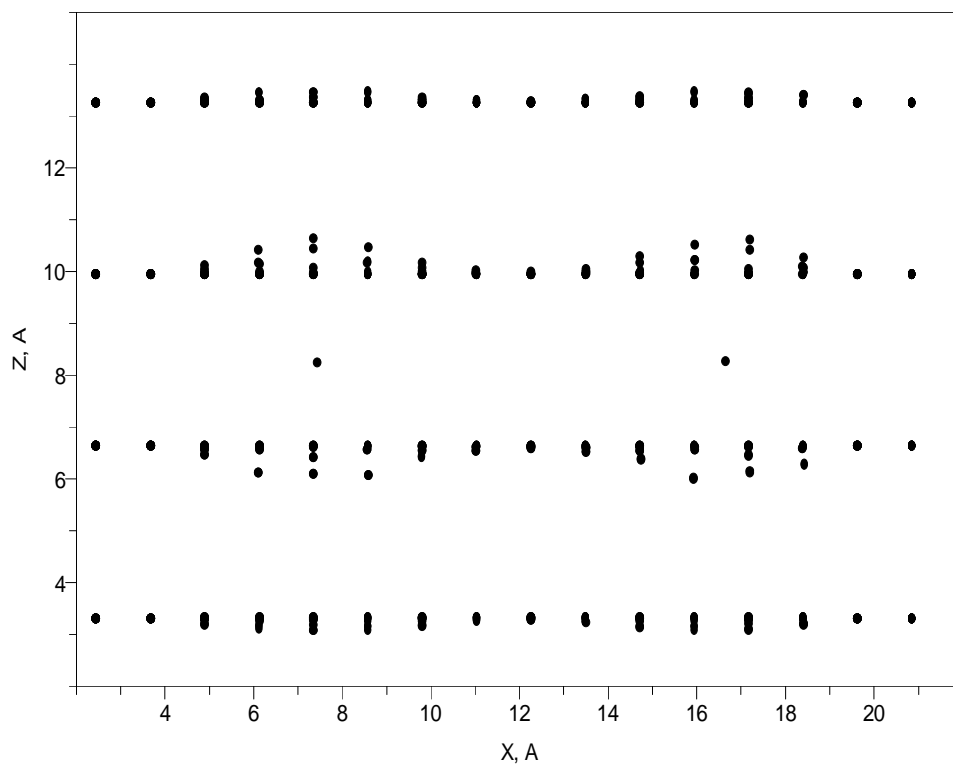


Fig.1a

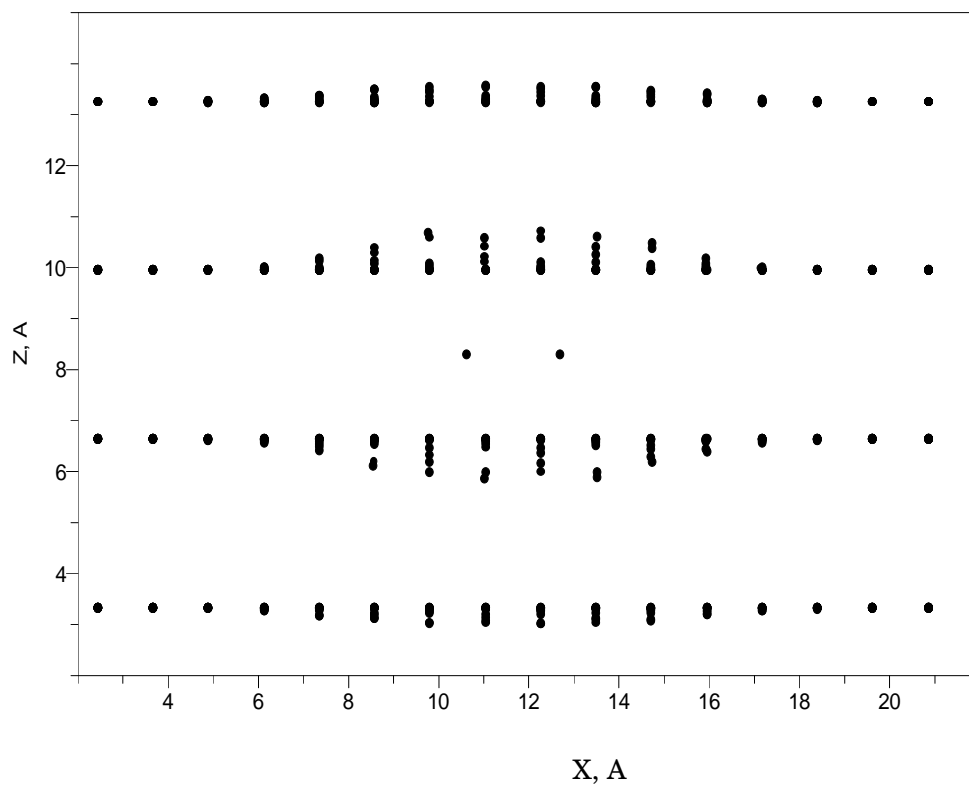


Fig.1b

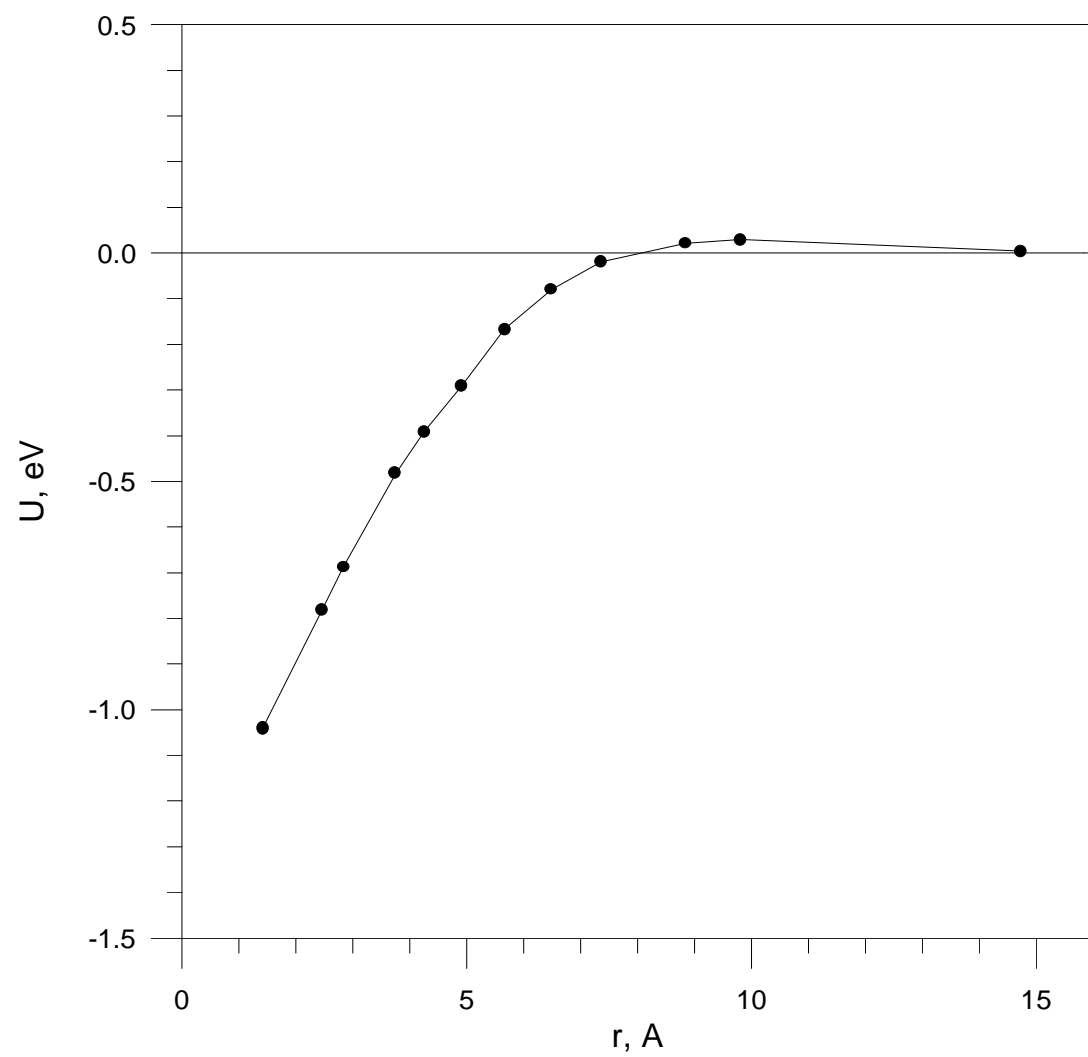


Fig.2

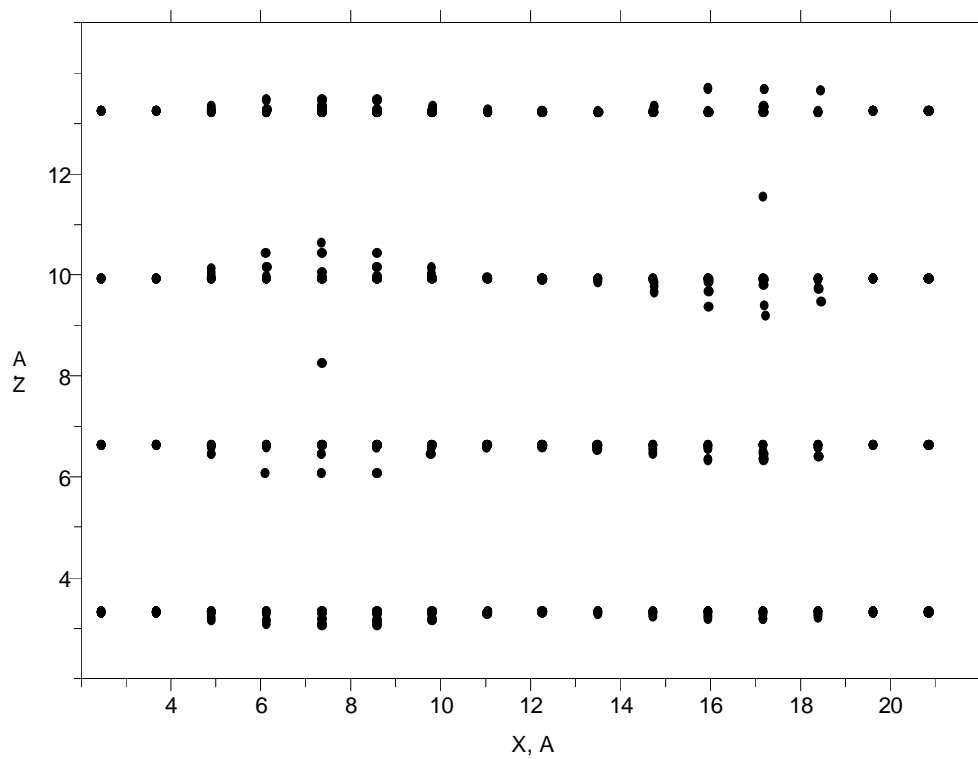


Fig.3a

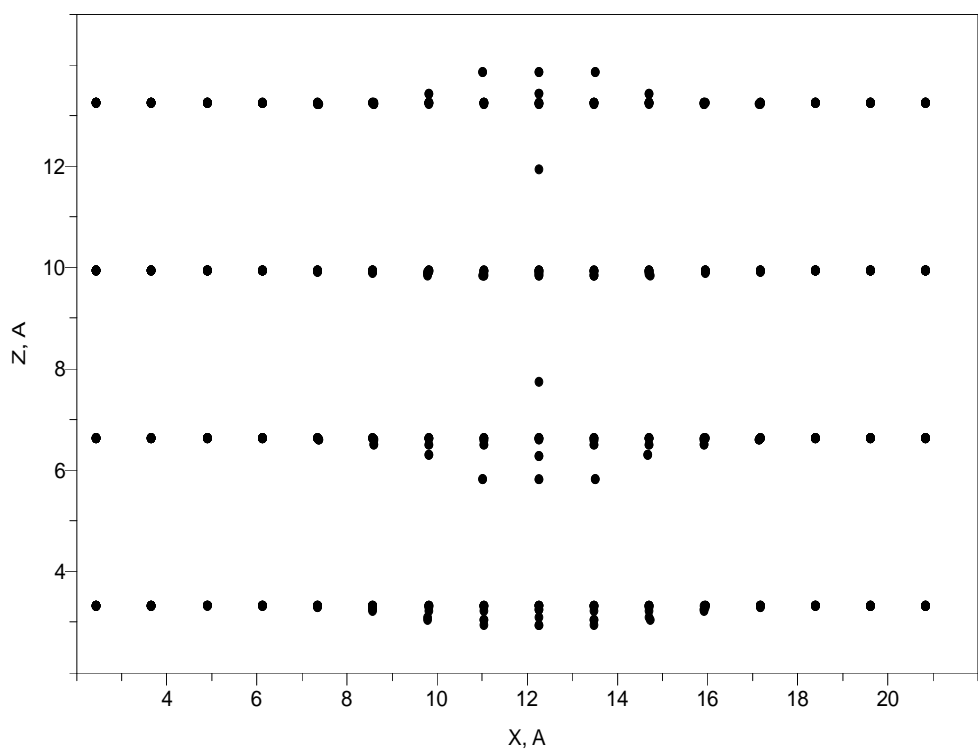


Fig.3b

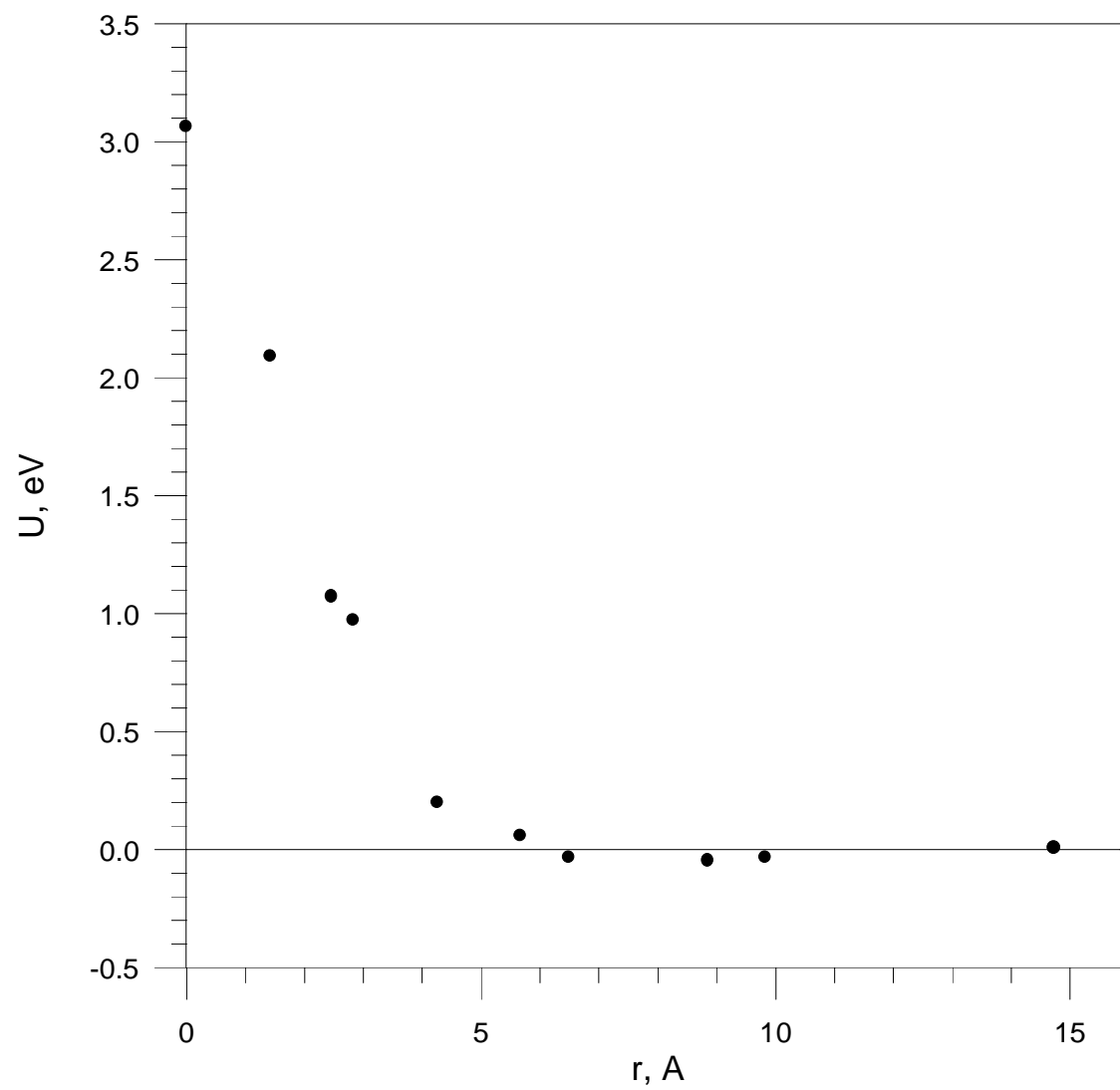
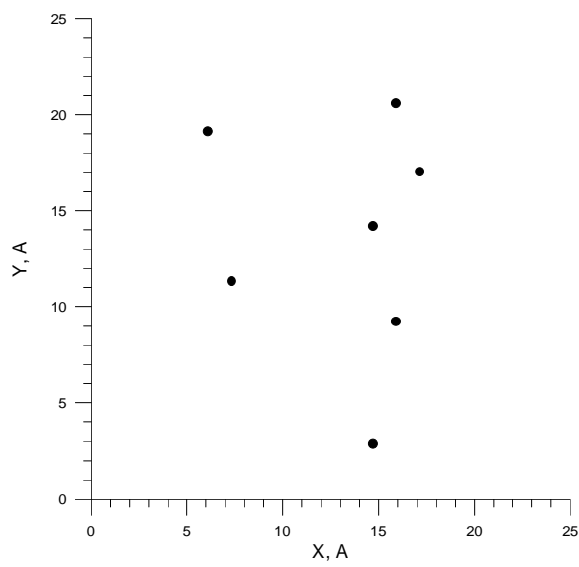
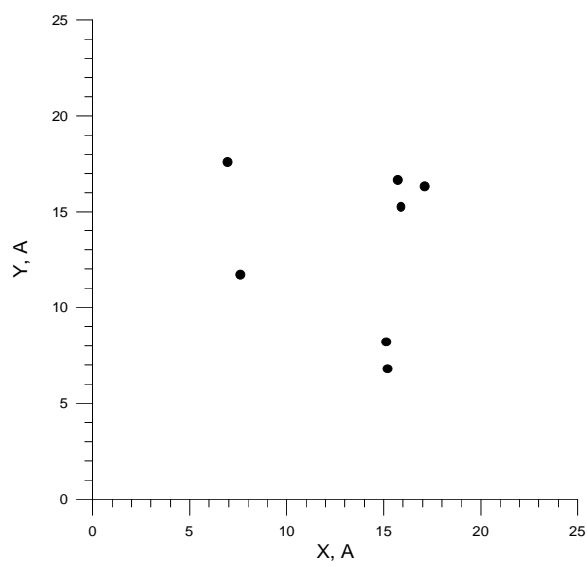


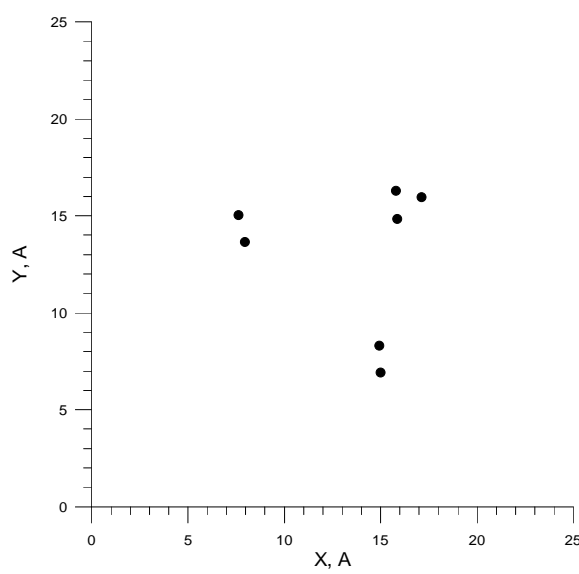
Fig.4



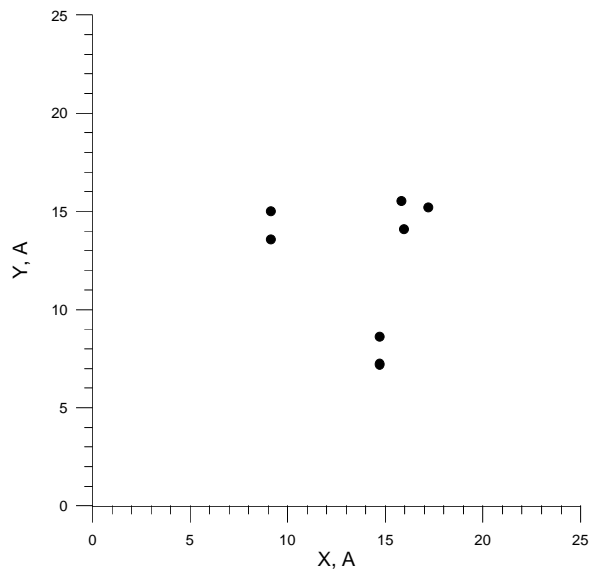
(A) $t=0$



(B) $t=100$

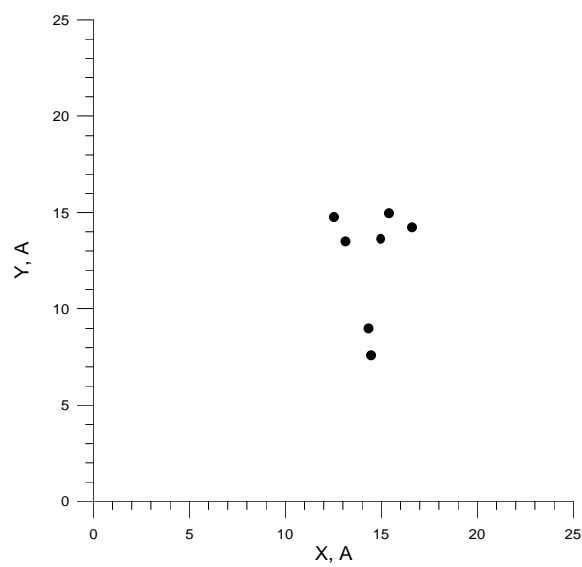


(C) $t=200$

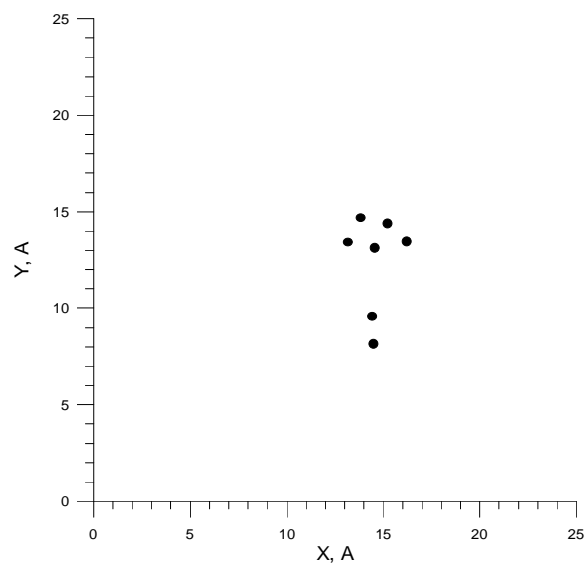


(D) $t=400$

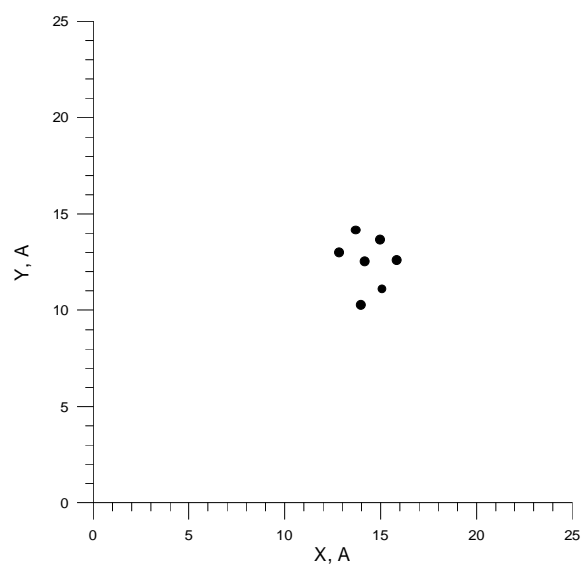
Fig.5 a-d



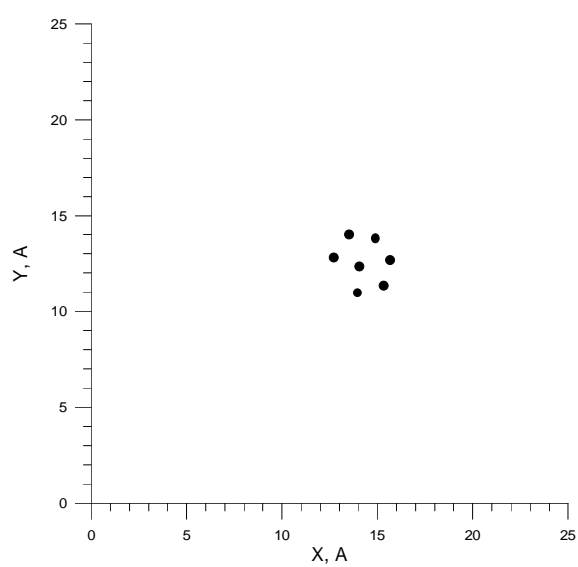
(E) $t=600$



(F) $t=800$

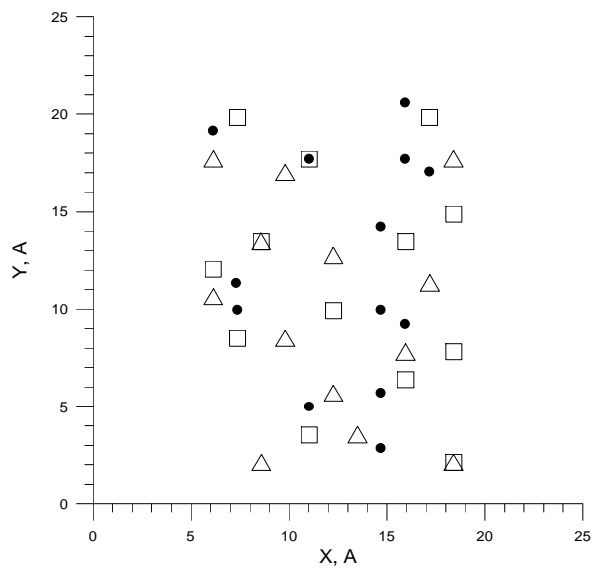


(G) $t=1200$

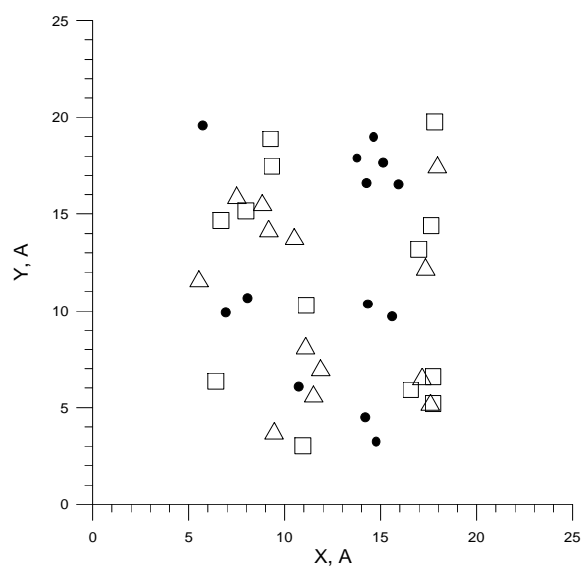


(H) $t=1600$

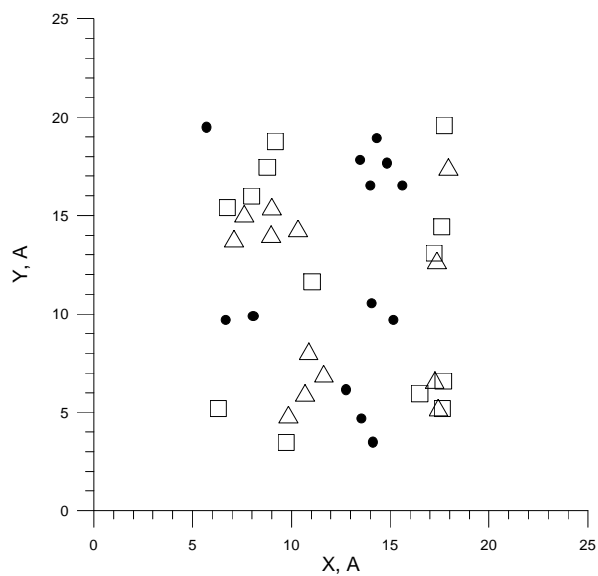
Fig.5 e-h



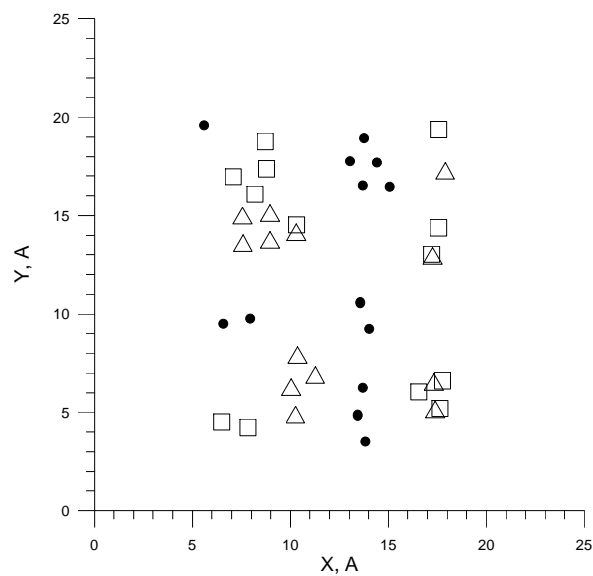
(A) $t=0$



(B) $t=50$

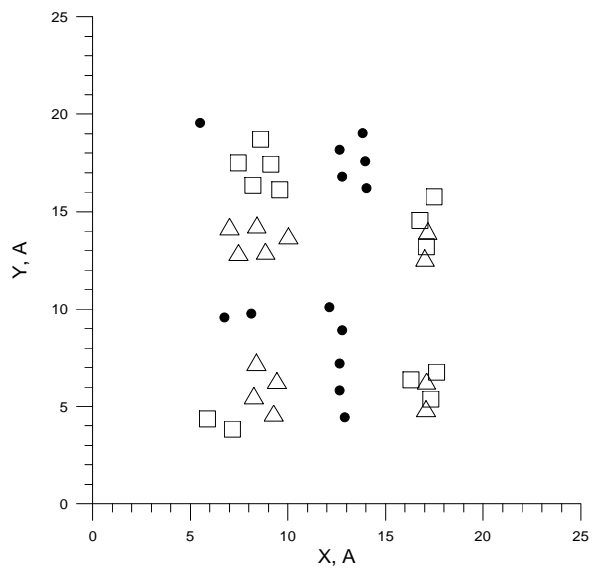


(C) $t=100$

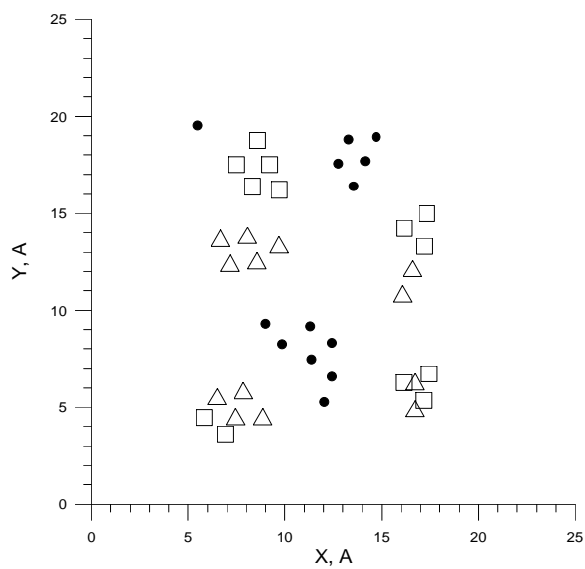


(D) $t=200$

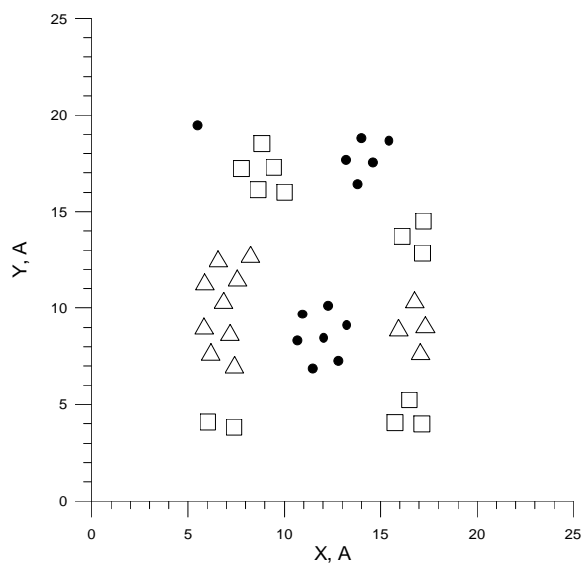
Fig.6 a-d



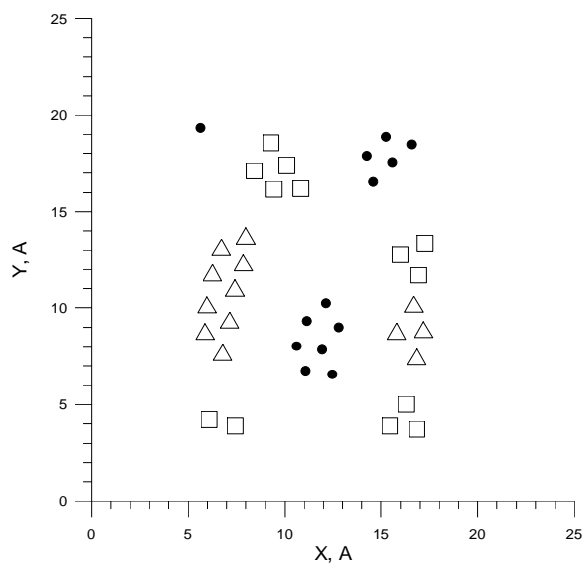
(E) $t=600$



(F) $t=1000$



(G) $t=2000$



(H) $t=5000$

Fig.6 e-h